Dynamic Evidence of Multiplicity in a Reactive Distillation Column for Ultra-Low Sulfur Diesel Production

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Abstract

The objective of the work is to analyze and predict the multiple steady states through dynamic analysis when the reactive distillation column is subject to different input disturbances. The dynamic simulations are carried out to analyze the open loop dynamic responses of the system using step changes in the manipulated variable (reflux ratio, holdup, hydrocarbon mixture feed stage, hydrocarbon mixture feed flowrate, reboiler duty) and recording the dynamic behaviour of the product conversions (dibenzothiophene and 4,6-dimethyldibenthiophene, called controlled variables). The magnitude of the change in the manipulated variables should be reduced to around 0.5% or less than its nominal value.

Keywords: reactive distillation, multiple steady states, HDS, dynamic simulation

1. Introduction

Conventional hydrotreating is a commercially proven refining process that passes a mixture of heated feedstock and hydrogen through a catalytic reactor to remove sulfur and other undesirable impurities. A review of the technologies for producing ultra-low sulfur diesel reveals that current technologies can be modified to produce diesel with less than 10 ppm sulfur. Nevertheless, only a small number of refineries currently produce diesel with sulfur in the 10 ppm range on a limited basis. The existence of the required technology does not ensure, however, that all refineries will have that technology in place in time to meet the new ultra-low sulfur diesel standards because these plants are characterized by a wide range of size, complexity, and quality of crude oil inputs.

An analysis of the operating conditions to obtain ultra-low sulfur diesel in a conventional trickle bed hydrodesulfurization (HDS) reactor (van Hasselt et al., 1999; Knudsen et al., 1999) suggests that reactive distillation could be an interesting

technological alternative for deep HDS of diesel. However, although reactive distillation has several advantages, incomplete understanding of the system specific non linear phenomena caused due to the complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalyzed processes) and chemical kinetics. Various operating parameters may very strongly influence on the process performance. This parametric sensitivity of the column leads to a complex dynamic behaviour of the system; for this reason, the increasing interest in reactive distillation has been accompanied by the development of various simulation algorithms related to the study of operation and control of the process (Abufares and Douglas, 1995; Monroy-Loperena et al., 2000; Sneesby et al., 1997a, 1997b). A key point is that the analysis of a single steady state (SSS) or multiple steady states (MSS) provides in which operating region (process operability) a reactive distillation column is operating, to understand how the column will respond to changes in operating variables (process controllability).

The objective of this work is to present an explanation of why the ultra-low sulfur diesel production by reactive distillation may yield MSS through dynamic simulation. We are interested on studying the effect of the operating conditions and parameter sensibility over the main variables to monitor or control hereinafter: the recalcitrant reactants conversion of the organo-sulfur compounds (as a measure of the variations in the composition of the sulfur-containing hydrocarbon feed stream) and the product purity (as a measure of the product quality: ultra-low sulfur diesel).

2. The HDS Reactive System

The sulfured-diesel has been modeled as a hydrocarbon mixture (HC) of four organo-sulfur compounds (thiophene, Th, benzothiophene, BT, dibenzothiophene, DBT, and 4,6-dimethyldibenthiophene, 4,6-DMDBT) and of C_{11}-C_{16} paraffin blend as solvent medium: n-undecane (n-C_{11}), n-dodecane (n-C_{12}), n-tridecane (n-C_{13}), n-tetradecane (n-C_{14}) and n-hexadecane (n-C_{16}).

In general, there are two reaction pathways for removal of sulfur from the organo-sulfur compounds as illustrated in Figures 1 and 2 for DBT and 4,6-DMDBT, respectively. Via the first pathway the sulfur atom is directly removed (hydrogenolysis) from the sulfured molecule. In the second pathway the aromatic ring is prehydrogenated and sulfur is subsequently removed (hydrogenation) by direct extraction. Both pathways occur in parallel employing different active sites of the catalyst surface. The HDS reactions for Th, BT and DBT progress via the hydrogenolysis pathway (Knudsen et al., 1999; Vanrysselberghe and Froment, 1996). When alkyl substitutes are attached to the carbon atoms adjacent to the sulfur atom, the rate for direct sulfur extraction is diminished whereas the sulfur removal rate via the hydrogenation route is relatively unaffected. CoMo/Al_2O_3 catalysts are better for desulfurization via the hidrogenolisis pathway, while the NiMo/Al_2O_3 catalysts are preferable for HDS of refinery streams that require extensive hydrogenation. Which reaction pathways predominates depends on the nature of the organo-sulfur compounds, the reaction conditions (H_2 and H_2S partial pressures), and the catalyst used.

On the other hand, it is also well known that around 80% of the HDS of 4,6-DMDBT goes by the hydrogenation pathway with conventional sulfide Ni-Mo catalysts (Bataille et al., 2000). Therefore, modeling desulfurization kinetics of actual hydrocarbon streams is quite complex due to the presence of a wide variety of sulfur compounds, all of which have different reactivity.
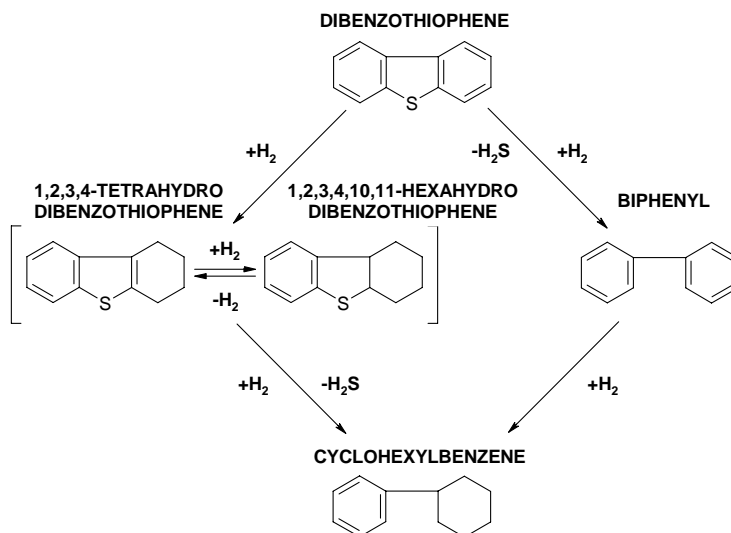

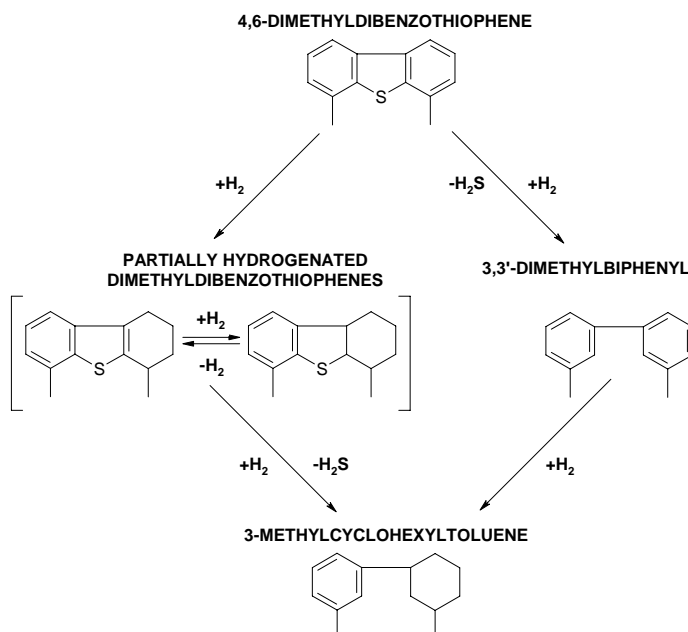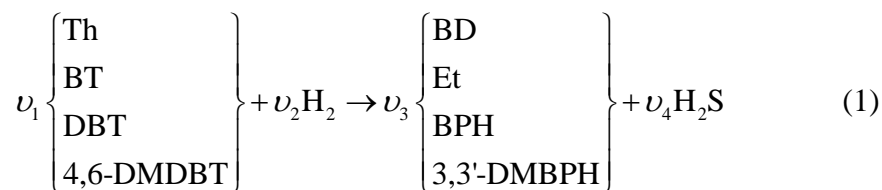Figure 1 Reaction pathways for HDS of DBT.

Figure 2 Reaction pathways for HDS of 4,6-DMDBT.

For practical design purposes, desulfurization for various species may be lumped into the following reactions for hydrogenolysis and hydrogenation, respectively:

$$\upsilon_1 \begin{Bmatrix} \text{Th} \\ \text{BT} \\ \text{DBT} \\ \text{4,6-DMDBT} \end{Bmatrix} + \upsilon_2\text{H}_2 \rightarrow \upsilon_3 \begin{Bmatrix} \text{BD} \\ \text{Et} \\ \text{BPH} \\ \text{3,3'-DMBPH} \end{Bmatrix} + \upsilon_4\text{H}_2\text{S} \tag{1}$$

$$\text{4,6-DMDBT} + 2\text{H}_2 \rightarrow \text{3-MCHT} + \text{H}_2\text{S} \tag{2}$$

Where BD represents butadiene; Et, ethylbenzene; BPH, biphenyl; 3-3'-DMBPH, dimethylbiphenyl; 3-MCHT, 3-methylcyclohexyltoluene; and υ_i are the appropriate stoichiometric coefficients.

The thermodynamic properties of the organo-sulfur compounds not reported in the literature are predicted through the group contribution method of Joback and Reid (1987). The kinetic expressions of the liquid phase HDS reactions (Eqs. 1-2) are taken from: Van Parijs and Froment (1986) for Th, Van Parijs et al. (1986) for BT, Broderick and Gates (1981) and Froment et al. (1994) for DBT, Vanrysselberghe and Froment (1996) and Vanrysselberghe et al. (1998) for 4,6-DMDBT.

3. Conceptual Design of the Reactive Distillation Column

The steady state design of the RDC described here is based on the work by Viveros-García et al. (2005), in which the optimal design was achieved through a rigorous optimizing procedure using Aspen Plus 11.1^{TM}. The application of reactive distillation concepts to the deep HDS of diesel were carried out through a thermodynamic analysis considering the following aspects: *i)* the volatility of the organo-sulfur compounds, *ii)* their different reactivities, and *iii)* the analysis of reactive residue curves. This configuration consists of 14 stages with two reactive zones and three non-reactive zones. It was fixed an operation pressure of 30 atm in the reactive column and a H₂/HC feed relation of 3 was used. The non-ideality of the system is accounted through the use of Peng-Robinson equation of state (Peng-Robinson, 1976). Table 1 shows the column configuration (Figure 3) details for the simulations. Target conversion of 99% for the DBT and 4,6-DMDBT were assumed as part of the design specifications.

Table 1 RDC design specifications.

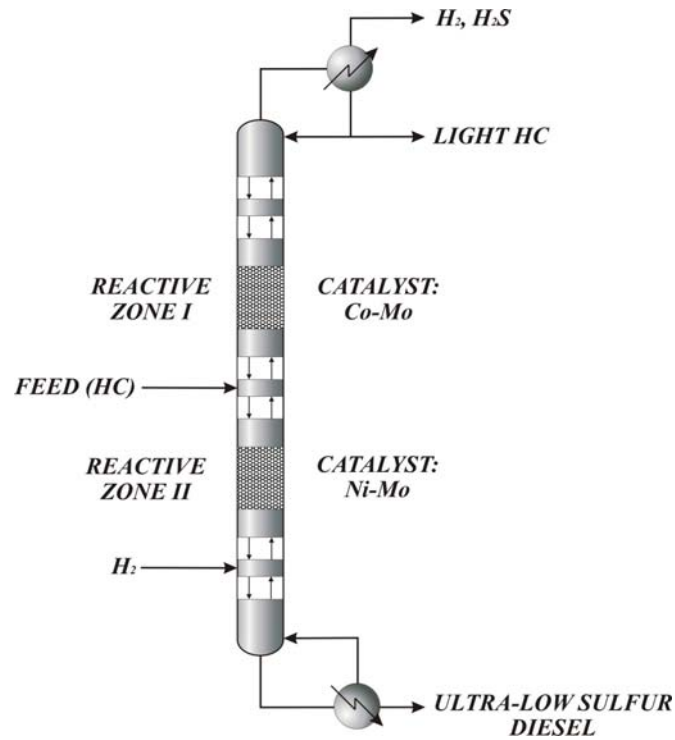| Specification	Value
Location of the stages of reactive zone I	5-7
Location of the stages of reactive zone II	10-12
HC feed stage	9
H₂ feed stage	12
H₂/HC feed relation	3
Molar reflux ratio	0.5
HC feed flowrate (kmol/h)	100
Distillate flowrate (kmol/h)	340
Holdup (kg catalyst)	10,000
Partial condenser temperature (K)	498.15

Figure 3 Conceptual design of a RDC for ultra-low sulfur diesel production.

4. Case Studies

With the purpose of analyzing the effect of the feed composition, the HDS reaction pathways, and the operating conditions, three case studies are considered as follows:

Case 1. HC feed composition A (given in Table 2), without including the 4,6-DMDBT, and following only the hydrogenolysis reaction pathway (Eq. 1).
Case 2. HC feed composition B (given in Table 2), which includes 4,6-DMDBT, and considering only the hydrogenolysis reaction pathway (Eq. 1).
Case 3. HC feed composition B (given in Table 2) and following both hydrogenolysis and hydrogenation reaction pathways (Eqs. 1-2).

Table 2 HC feed composition.

Component	Feed A (Mole fraction)	Feed B (Mole fraction)
Th	0.0087	0.0080
BT	0.0087	0.0080
DBT	0.1	0.1000
4,6-DMDBT	0.0	0.0200
$n\text{-}C_{11}$	0.4966	0.4890
$n\text{-}C_{12}$	0.3166	0.3160
$n\text{-}C_{13}$	0.0089	0.0080
$n\text{-}C_{14}$	0.0015	0.0010
$n\text{-}C_{16}$	0.0589	0.0500

5. Analysis of Steady State Multiplicity

The MSS is analyzed through bifurcation diagrams, which are built using a continuation method (Guckenheimer and Holmes, 1990), raking the steady state of the model when the value of a bifurcation parameter is increased or decreased. In fact, two multiplicity types can be found: input multiplicity and output multiplicity. Input multiplicity is associated with unusual, unexpected or inverse columns responses (Sneesby et al., 1998). It occurs when two or more unique sets of input variables produce the same out condition. Output multiplicity occurs when one set of input variables results in two or more unique and independent sets of output variables (Sneesby et al., 1998). Moreover, a combined input-output multiplicity may be also encountered. Next the effect of the DBT kinetic reaction rate and some operating conditions (holdup and reflux ratio) are discussed in the generation of SSS or MSS.

Effect of the DBT kinetic reaction rate. In order to study this effect, Case 1 is considered. The two following kinetic expressions for the hydrogenolysis reaction of DBT are studied:

$$r_{3,\sigma} = \frac{k' K_{DBT} K_{H_2} C_{DBT} C_{H_2}}{\left(1 + K_{DBT} C_{DBT} + K_{H_2S} C_{H_2S}\right)^2 \left(1 + K_{H_2} C_{H_2}\right)} \qquad (3)$$

$$r_{3,\sigma} = \frac{k_1 K_{DBT,\sigma} K_{H_2,\sigma} C_{DBT} C_{H_2}}{\left(1 + K_{DBT,\sigma} C_{DBT} + \sqrt{K_{H_2,\sigma} C_{H_2}} + K_{H_2S,\sigma} \dfrac{C_{H_2S}}{C_{H_2}}\right)^3} \qquad (4)$$

The kinetic constants for these expressions are given in Broderick and Gates (1981) and Froment et al. (1994), respectively. Bifurcation diagrams were built using both kinetic expressions and for most of the operating conditions (as bifurcation parameters): holdup, reflux ratio, HC feed stage, HC feed flow, H_2 feed flow, distillate ratio, condenser temperature and DBT feed composition. The main variables that affect the steady state behaviuor changing drastically the final elimination of sulfur compounds were: holdup, reflux ratio, HC feed stage, and HC feed flowrate (as shown in Figures 4a-4b); while the other variables do not modify significantly the final conversion. Moreover, all the bifurcation diagrams exhibited no evidence of multiplicity (i.e. only SSS). According to Figures 4a-4b, the DBT kinetic reaction does not affect significantly the final DBT conversion. From the results, it can be observed that the holdup (Figure 4a) must be greater than 1,000 Kg to keep a DBT conversion around 99%; while below 1,000 Kg there is a strong decline of the conversion. Something similar happened with the reflux ratio (Figure 4b), its value must be greater than 0.4, otherwise with lower values there is a decrease in the DBT conversion.

Effect of the holdup. Figures 4a, 5a and 6a show the effect of varying the holdup in the RDC for the three case studies, respectively. As aforementioned Case 1 does not present MSS, but Cases 2 and 3 reveal the existence of MSS in the HDS system:

output multiplicity for DBT conversion and input-output multiplicity for 4,6-DMDBT conversion. For Case 2 (Figures 5a) at holdups between 7,150 and 8,500 Kg and for Case 3 (Figure 6a) at holdups between 4,300 and 6,650 Kg, there are three steady state solutions that for a same value of the holdup, and each solution corresponds to different conversions of DBT and 4,6-DMDBT. In addition, as 4,6-DMDBT conversion presents both input and output multiplicity, this implies that a same 4,6-DMDBT conversion can be obtained at two different values of the holdup. When only a SSS is present, such steady state is stable. On the other hand, when three steady states are present, the ones corresponding to low and high conversion are stable; while the other one corresponding to middle conversion is unstable. Along the branch containing unstable steady state solutions, open loop operation is not possible and the control of unstable states becomes more difficult than controlling stable states. Meaning that the stable steady states of the upper branch (i.e. with high conversion) outside the MSS region are better to be selected as operating points (set points). According to this, the holdup should be kept in a value greater than: (a) 1,000 Kg for Case 1, (b) 8,500 Kg for Case 2, and (c) 6,650 Kg for Case 3. Of course, it must keep in mind that the more realistic case study is Case 3, as it considers a diesel composition with all four organo-sulfur compounds and a complete reaction scheme.

Effect of the reflux ratio. The variation of the reflux ratio as bifurcation parameter is shown in Figures 4b, 5b and 6b for the three case studies respectively. A similar behaviuor to the holdup variation is obtained: Case 1 does not present MSS, while Cases 2 and 3 present output multiplicity for DBT conversion and input-output multiplicity for 4,6-DMDBT conversion. The MSS region is found between reflux ratio values of 0.435 and 0.35 for Case 2, and 0.22 and 0.345 for Case 3. Meaning that stable steady states with high conversion outside the MSS region are located in reflux ratio values greater than: (a) 0.4 for Case 1, (b) 0.435 for Case 2, and (c) 0.345 for Case 3; which are values very close. The variation of the reflux ratio as bifurcation parameter is shown in Figures 7b, 8b and 9b the three case studies respectively. A similar behavior to the holdup variation is obtained: Case 1 does not present MSS, while Cases 2 and 3 present output multiplicity for DBT conversion and input-output multiplicity for 4,6-DMDBT conversion. The MSS region is found between reflux ratio values of 0.435 and 0.35 for Case 2, and 0.22 and 0.345 for Case 3. Meaning that stable steady states with high conversion outside the MSS region are located in reflux ratio values greater than: (a) 0.4 for Case 1, (b) 0.435 for Case 2, and (c) 0.345 for Case 3; which are values very close.
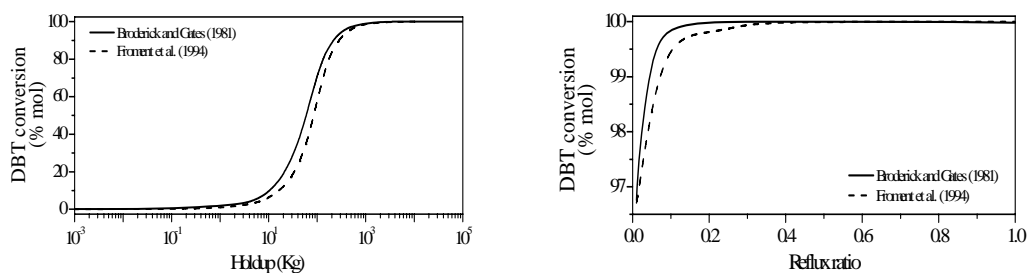

Figure 4 Bifurcation diagrams using two kinetic expressions for DBT in case 1: (a) holdup, (b) reflux ratio.
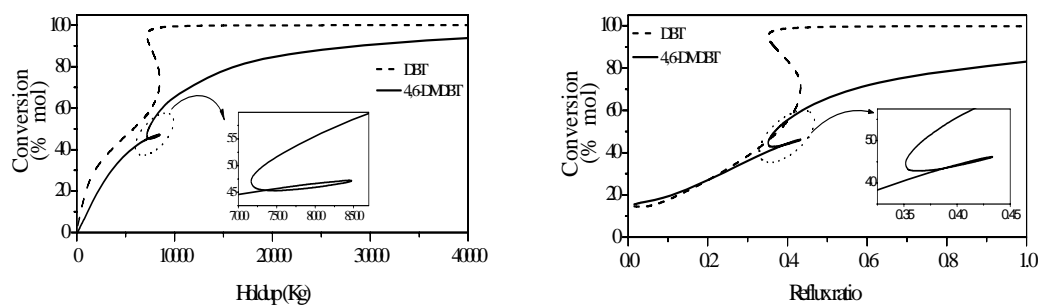
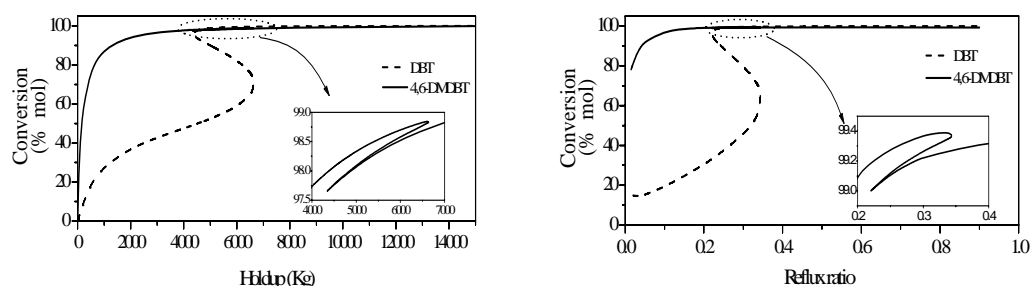Figure 5 Bifurcation diagrams for Case 2: (a) holdup, (b) reflux ratio.

Figure 6 Bifurcation diagrams for Case 3: (a) holdup, (b) reflux ratio.

6. Dynamic Simulation

Process design is traditionally performed in steady state, but the operation of complex chemical processes in dynamic mode must be considered when the technology assessment to be chosen is the priority. Reactive distillation seems to be an attractive technology in the synthesis of several chemicals, being a process highly complex when considering dynamic mode. This kind of hybrid column can show a non usual dynamic behaviour with limited control characteristics in a way that the benefits which come with its choice can not be effective without an appropriate control strategy in some cases. Thus, since reactive distillation can show a great variety of dynamic phenomena, it is very important to create subsides through the dynamic simulation in order to understand this process in an ample way, as a powerful toll in control system design, unit startup and shutdown, scale up, failure analysis, etc.

Aspen Dynamics 11.1 [TM] commercial simulator is used to perform the simulations in the present work. The equilibrium stage model is used in the simulation with bubble cap stages in the non-reactive zones and catalytic Rasching Rings in the reactive zones. The residence time of each device internal is about 5 min. This design is intended to have a high holdup and liquid phase residence time so that the regime of operation at each device internal is in the bubbly flow regime. For the dynamic behaviour analysis, it was found that the holdup, sulfur composition in the HC feed stream and the H_2/HC feed ratio determines the final steady state archived. For example, it could be noted when the holdup is set at high values, a high conversion steady state is achieved independently of the HC feed flow; while if the reflux ratio is reduce drastically higher amounts of catalyst are required to achieve a high conversion steady state.

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7. Conclusions

The rigorous analysis of steady state multiplicity of a reaction-separation process for deep HDS of diesel has been presented. The effect of several operation conditions were analyzed, for instance changes in holdup and reflux ratio. According to the analysis, feasibility regions to obtain high conversions can be guaranteed selecting those operation conditions outside of the multiplicity region (i.e. in the upper stable branch of the bifurcation diagrams), for example: with high values of holdup, moderate values of reflux ratio and the HC feed stage located in the reactive zones or between them. Nevertheless, from an industrial point of view, frequently is desirable to operate the process in the region of unstable multiplicity, since the reaction rate can allow high conversion and productivity, guaranteeing moderate temperatures that prevent the side reactions or the deactivation of the catalyst. Therefore, the implementation of a control is necessary to reach the unstable steady state, implying the selection of input-output control. In this case, the analysis of multiplicity is outstanding for control purposes, since the possible inputs (HC feed flow, reflux ratio, condenser temperature, etc.) have been studied in this work as bifurcation parameters.

Actually the dynamic simulations continue being carried out to determine open loop responses; this backwardness of results is due, because the dynamics of this column is very difficult and complex to carry out. We suppose that the main problem resides in the complex HDS reactive system, implying that the some design parameter or hydrodynamic not this fulfilling the convergence restrictions. Therefore the general conclusion is that one way to overcome the hardware and controllability design conflicts in the RDC, while maintaining the benefits of *in-situ* separation with reaction, is to employ the *Distillation-Side Reactor Concept*, DSRC, (Ojeda Nava et al., 2004; Kaymak and Luyben, 2007).

8. References

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